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Applicant

SMITH, Robert, Terence et al

1. The designated Office is hereby notified of its election made:



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30 April 1998 (30.04.98)



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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/GB97/02705 (22) International Filing Date: 1 October 1997 (01.10.97) (30) Priority Data: 9620752.7 4 October 1996 (04.10.96) GB (71) Applicant (for all designated States except US): DYTECH CORPORATION LTD. [GB/GB]; Stopes Road, Stannington, Sheffield S6 6BY (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): SMITH, Robert, Terence [GB/GB]; 103 East Bawtry Road, Brecks, Rotherham S60 4BX (GB). SAMBROOK, Rodney, Martin [GB/GB]; 11 Brookfields, Calver, Sheffield S30 1XA (GB). (74) Agent: SHAW, Laurence; Laurence Shaw & Associates, Metropolitan House, 5th floor, 1 Hagley Road, Edgbaston, Birmingham B16 8TG (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PRODUCTION OF POROUS ARTICLES		
(57) Abstract An aqueous dispersion of ceramic particles and containing a polymerisable monomer was foamed before polymerisation, e.g. using a catalyst and initiator, was started.		

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PRODUCTION OF POROUS ARTICLES

The invention relates to the production of articles of controlled porosity.

In our European patent B-0598783 (Agent's ref: P00914EP) there is described and claimed a method of making a porous refractory article composed of refractory particles, the method comprising the steps of:

- a) forming a dispersion comprising particles in a liquid carrier and containing a polymerisable monomeric material
- b) introducing gas into the dispersion,
- c) polymerising the foamed structure,
- d) drying, to remove the liquid carrier to provide a solid article having pores derived from the bubbles; and
- e) firing to remove the organic binder and to provide a ceramic bond.

Preferably the monomeric material is selected to polymerise by cross linking, whereby the liquid carrier and ceramic particles are held within the polymerised structure.

The method of this prior patent is arranged to produce a variety of useful articles such as catalyst supports, flame supports; gas filters; air fresheners; ceramic armour; diesel particulate traps; insulation materials; artificial parts for the body; metal filters, reusable filters; liquid filters; storage and transportation for flammable and/or toxic materials,

humidity sensors, chromatography; filter candles for filtration of hot combustion gases, diaphragms, membranes, refractory separators, phase dividers and electrolytes for high temperature fuel cells.

In our patent publication WO95/30631 (PCT/GB95/01063, Agents Ref. P01204PCT) there is described and claimed a method of making a porous refractory article, the method comprising the steps of:

- forming an aqueous dispersion of refractory particles including a polymerisable monomer component which on polymerisation generates an exotherm
- adding a thermally activated gas generating substance
- adding agents such as initiator and/or catalyst to cause the polymerisation
- adjusting the temperature and/or pressure so that the gas generating substance generates the gas before or during the initial stage of polymerisation of the monomer component whereby the gas forms bubbles which under the heat of the exotherm interconnect to form an interconnected open pore structure.

By controlling the temperature and pressure the decomposition rate of the gas generating substance is controlled. This in turn provides a means of controlling the density of the end product.

It is one object of the invention to provide a method of making a porous article having controlled levels of porosity, interconnectivity, pore size, and mechanical properties suitable for use in various applications.

In one aspect the invention provides a method of making a porous article composed of bonded particles, the method comprising the steps of:

- a) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
- b) forming a foam of the dispersion;
- c) polymerising the foamed structure;
- d) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles, and
- e) firing the article to remove the organic binder and provide a ceramic bond

characterised in that small bubbles of gas are introduced in the dispersion with agitation to form the foam and are allowed or caused to coalesce before the polymerisation.

The dispersion comprises particles having an average particle size less than about 5 micrometres and preferably 95% of the particles will be less than about 2 micrometres.

If the particles are larger than this size than the particles tend to settle or sediment. However, the particles can be much larger, say 100 micrometres or more, in which case agents will be present to control undesired settling; polymerisation of monomers is a suitable means of preventing settling. The particles will be chosen according to the intended end use. As will be explained later, for the preferred use hydroxyapatite is present either alone or with other particles. The other particles can include both oxides and non-oxides such as alumina, mullite, silicon carbide, silicon nitride, zirconia, titanium oxide and the like.

The content of the solids in the dispersion will tend to be about 10% by weight as a minimum and about 90% by weight as a maximum; a preferred range is from about 40% to about 80% by weight.

Conveniently the liquid carrier is water but it may be organic, e.g. alcohol, glycol or the like; or a mixture.

In order to produce a dispersion with the required solids loading and a suitable rheology, it is preferred to add dispersing agents to the suspension. The dispersing agents are commonly used throughout the ceramic industry and suitable agents in each case can be determined by the man skilled in the art. The colloidal stability may be controlled by the adjustment of the pH, in addition to or alternating to the dispersion agents.

Advantageously surfactants (which can be cationic, anionic or non-ionic) are present in the dispersion. In low viscosity systems where the ability of a system to foam is controlled by the surface tension, the surfactant type and concentration can have a direct influence not only on the level of porosity within the system but also the pore size and the interconnectivity. The concentration of surfactant can be used to influence the bubble size within a foam and the rate of coalescence, both of which can be used to influence the final pore size.

By controlling the rheology of the suspension it is possible to influence the rate of coalescence of the foam structure. A slurry which exhibits a low degree of pseudoplasticity coupled with a low bulk viscosity is susceptible to foam collapse and rapid bubble growth. In contrast a slurry which exhibits a high degree of pseudoplasticity is subject to long term stability and a less rapid bubble growth although at an acceptable level. As the bulk viscosity of the system increases the controlling effect of the surfactant diminishes.

Another factor which influences the growth of the foam structure is the period before the onset of polymerisation. This period can be controlled by the addition levels of the initiator and catalyst. By controlling these levels as well as the oxygen concentration within the foaming gas the length of time before polymerisation starts can be controlled between an instantaneous polymerisation and one which starts after a period, which can be up to 20 minutes or more. Our evaluations suggest that this period has a major influence on cell structure where the porous article is to be used as a bone substitute.

In a further feature of the invention the process of increasing the cell size within a foam can be encouraged by the application of a partial vacuum to a foam before the commencement of polymerisation until after the end of polymerisation. At the end of polymerisation the stable foam is brought back to atmospheric pressure. This additional step to the foaming process can be used to increase the rate at which the final desired large cell size can be achieved.

Other additives may be present, e.g. viscosity control agents, reinforcing fibres or particles, retarders for polymerisation; and the like.

The bubbles of gas may be introduced in any convenient way, although the preferred methods are listed in our previous patent. The gas used for foaming can be air, although an inert foaming gas such as nitrogen or argon is preferred. To produce a foam with a large pore structure and a high degree of porosity, one could either introduce bubbles of the correct size and quantity into the suspension or cause smaller bubbles to grow by a process of coalescence. The latter is preferred at the moment.

In order to produce the small bubbles within the foam mechanical agitation is preferred.

Our investigations have shown that the structure of the foam can be broken into four distinctly different areas:

- the cells or bubbles

- the struts
- the windows, and finally
- the particulate microstructure

These structures can be seen in Figure 1 of the accompanying drawings and are explained as follows.

A number of cells can be seen in the left hand photo in Figure 1. These cells are formed as a result of introducing a gaseous phase into the ceramic suspension. Where these cells touch there is a tendency for the cell to change shape to maximise the packing density and for the slurry to drain from the point of contact towards the strut.

A strut can be seen in the top right hand photo in Figure 1. These struts are the building block for the foam structure. At the point of contact between each cell a thin film of liquid exists. During the later gelling and binder burnout steps this film is removed to leave what we call the cell "windows". These are the connecting holes which interlink adjacent cells and can be clearly seen in the left hand photo in Figure 1.

The final structure is that which forms the cell walls and struts.

It is a feature of the invention that the final articles formed consist essentially of the starting ceramic materials only, so avoiding the need for the removal of residual secondary e.g. inorganic binders. The article can thus consist of ingredients acceptable for medical use, e.g. as bone grafts for orthopaedic, surgical, dental and like uses both for humans and animals. There will always be a need to replace bone lost as a consequence of traumatic or non-traumatic events. Bone substitute materials are

available and approved for clinical use. These materials have been successfully used in orthopaedics, dentistry and facial plastic surgery. Among the types of bone graft materials used, particular interest has been shown in the porous types which can provide a scaffold for in growth of connective tissue and bone. Studies have shown that pore sizes less than 10 micrometre prevent ingrowth of cells, pore sizes of 15 to 50 micrometre encourages fibrovascular ingrowth; pore sizes of 50-150 micrometre result in osteoid formation; and pore sizes greater than 150 micrometre facilitate the ingrowth of mineralized bone. Different approaches have been taken to try and mimic the hydroxyapatite frame work within both the cortical and cancellous bone. One material is based on the conversion of a coralline structure to hydroxyapatite material. With this process the selection of the coral with the correct pore structure is imperative before conversion takes place. Two corals were eventually selected exhibiting two different pore structures. These two pore structures are intended to replicate the different structures in cortical and cancellous bone. It is a feature of this invention that synthetic articles made by the method may be used as bone graft materials of high acceptability.

Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ is an ideal candidate starting material. This material belongs to a group of calcium phosphates which are being considered as bone substitute materials. The invention is applicable to hydroxyapatite and any other calcium phosphate (where the Ca/P atomic ratio may vary widely). In addition to this group of materials it may be advantageous to create an interconnected structure in another ceramic material such as alumina or zirconia for mechanical property reasons and either use the material as produced, or coated with a more bioactive material such

as hydroxyapatite. It is another feature of this invention that the materials known as "Bioglass" could be converted in highly porous structures using this method.

The polymerisation preferably proceeds by crosslinking of reactive organic monomers. Examples include acrylates, such as ammonium acrylate or hydroxyethyl methacrylate; or the like. Preferably the monomers are dissolved in water or other liquid carrier to give a premix solution. To this solution are added an initiator and either heat or a catalyst are used to induce free radical vinyl polymerisation. In another variation, the dispersion includes a monosaccharide such as galactose, which can be condensed to form a dimer, trimer or polymer, to have the same effect.

The foamed composition may be allowed or caused to acquire sufficient green strength to allow it to be moved from the parent container or mould. The composition may be subjected to drying to drive off the liquid. In the case of water, drying can be carried out below about 100°C in an oven or using high frequency drying equipment.

The pore sizes in the formed article can be controlled remarkable uniform to yield a material with a pre-determined pore size and level of interconnectivity. The true porosity may range from about 20% to about 95%. The article formed is relatively robust after polymerisation and strong enough to be machined after removal of the liquid carrier.

The firing temperature and duration are selected according to the nature of the particles, e.g. alumina generally requires a higher sintering temperature than hydroxyapatite.

In one more specific aspect the invention provides a method of making a porous article composed of bonded particles, the method comprising the steps of:

- a) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
- b) forming a foam of the dispersion;
- c) polymerising the foamed structure
- d) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles, and
- e) firing the article to remove the organic binder and provide a ceramic bond.

characterised in that small bubbles of gas are introduced in the dispersion with agitation to form the foam and are allowed or caused to coalesce before the polymerisation, and in that the firing is carried out at a temperature appropriate to the growth of bone cells.

It is a feature of this invention to provide an article having a highly microporous structure if the sintering procedure is controlled. This microporous structure can have advantages in certain applications e.g. it may be infilled with certain drugs such as

antibiotics or growth factors, to act as a slow release agent at the site of an implant and it appears to encourage the easy attachment of in-growing bone cells compared to a dense microstructure.

The formed article may be in a variety of shapes, e.g. in the form of granules, bars, cylinders or rods, blocks or the like.

In order that the invention may be well understood it will now be described by way of illustration only by reference to the following examples and micrographs:

Example I

Hydroxyapatite powder, ammonium acrylate monomer, methylenebisacrylamide, water, the ammonium salt of polyacrylate and the ammonium salt of polymethacrylate were mixed together to form a slurry which was subjected to a high shear mixer in order to remove any agglomerates within the slurry. This was transferred to a glove box within which the oxygen concentration was approx. 0.1%. A surfactant TERGITOL TMN10 was introduced into the slurry and the whole was agitated in a mixer designed to introduce air so that a foam will be formed. The amount by which the ceramic solid is foamed is dependant on the final density required, the solids content of the slurry and the shrinkage which will occur at the later stages of drying and firing. The amount of surfactant added determines the extent of foaming, and this was selected to achieve the required final density. Once the foam density was achieved, ammonium persulphate (initiator) and tetramethylethylenediamine (catalyst)

were injected into the foam to cause the acrylate monomer to start to polymerise. The time before the onset of polymerisation was about 1.5 minutes.

The mixture was restirred and allowed to stand. Polymerisation began after about 1.5 minutes. A photo of the microstructure produced after an idle time of 1.5 minutes is shown in Figure 2. Once polymerised the foam was removed from the mould and allowed to dry at room temperature for 2 days before being forced dried at 60° C in an oven.

At this point the "green" ceramic can easily be machined into the desired shape. The "green" article was heated in a furnace to remove the organic binder and to cause the ceramic microstructure to densify. The sample was split in two and fired at two different temperatures. Sample 1 shown in Figure 3 and sample 2 in Figure 4 were fired at 1250° C for 2 hrs and 1350° C for 2 hrs respectively. It can be seen that the degree of microstructural densification can be adjusted with the sintering conditions. Sample 1 exhibits a highly connected microstructure whereas the microstructural porosity has been removed in sample 2. Live human bone cells were cultured. Both samples 1 and 2 were immersed in the cultures and Figures 5 and 6 show the results after 36 hrs immersion for sample 1 and 2 respectively. The bone cells can be clearly seen on the surface of the cell walls. From these Figures it appears easier for the bone to grow within the undersintered microstructure than the fully densified structure.

Example II

The method of Example I was repeated except that the rate of addition of the initiator and the catalyst were selected so that the time before onset of polymerisation was 16 minutes instead of 1.5 minutes. A highly porous foam exhibiting a larger cell size as shown in Figure 7 resulted. It can be seen from the different Figures that the time before the onset of polymerisation has had a major influence on the cell structure.

The Figures of the accompanying drawings are microphotographs as follows:

Figure 1 is a general foam;

Figure 2 is a foam produced in Example I taken after an idle time of 1.5 minutes;

Figure 3 is the polymerised foam of Example I fired at 1250°C for 2 hours;

Figure 4 is the polymerised foam of Example I fired at 1350°C for 2 hours;

Figure 5 is the fired product shown in Figure 3 after being immersed in a bone cell culture for 36 hours;

Figure 6 is the fired product shown in Figure 4 after being immersed in a bone cell culture for 36 hours; and

Figure 7 is the foam produced in Example II.

CLAIMS

1. A method of making a porous article composed of bonded particles (such as hydroxyapatite or the like) the method comprising the steps of:
 - a) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
 - b) forming a foam of the dispersion;
 - c) polymerising the foamed structure;
 - d) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles, and
 - e) firing the article to remove the organic binder and provide a ceramic bond

characterised in that small bubbles of gas are introduced in the dispersion with agitation to form the foam and are allowed to caused to coalesce before the polymerisation of the monomeric material.
2. A method according to Claim 1, wherein the dispersion comprises particles having an average particle size less than 5 micrometres and preferably 95% of the particles are less than 2 micrometres.

3. A method according to Claim 1 or 2, wherein the particles are hydroxyapatite, oxides and non-oxides such as alumina, mullite, silicon carbide, silicon nitride, zirconia, titanium oxide; and the like.
4. A method according to any preceding Claim, wherein the content of the solids in the dispersion is 10% to 90% by weight.
5. A method according to Claim 4, wherein the content of solids is 40% to 80% by weight.
6. A method according to any preceding Claim, wherein the liquid carrier is water or organic liquid or a mixture.
7. A method according to any preceding Claim, including the step of adding a dispersing agent to the dispersion.
8. A method according to any preceding Claim including the step of controlling the onset of polymerisation by adjustment of the addition levels of the initiator and catalyst for polymerisation of the monomer.
9. A method according to any preceding Claim, wherein the onset of polymerisation is controlled by adjustment of the concentration of oxygen.
10. A method according to Claim 8 or 9, wherein the period until onset of polymerisation is between an instantaneous polymerisation and 20 minutes.
11. A method according to any preceding Claim, including the step of applying a partial vacuum to a foam before the commencement of polymerisation until

after the end of polymerisation, after which the foam is brought back to atmospheric pressure.

12. A method according to any preceding Claim, wherein the product is subjected to drying and firing to form a porous ceramic article.
13. A method according to Claim 12, including the subsequent step of growing bone cells in the porous ceramic product.
14. A method according to Claim 12, wherein the ceramic article has pore sizes greater than 150 micrometres.
15. A method according to Claim 12, including adding a drug to the pores of the article.
16. A method of making a porous article composed of bonded particles, the method comprising the steps of:
 - a) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
 - b) forming a foam dispersion;
 - c) polymerising the foamed structure;
 - d) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles, and

- e) firing the article to remove the organic binder and provide a ceramic bond

characterised in that small bubbles of gas are introduced in the dispersion with agitation to form the foam and are allowed or caused to coalesce before the polymerisation, and in that the firing is carried out at a temperature appropriate to the growth of bone cells.

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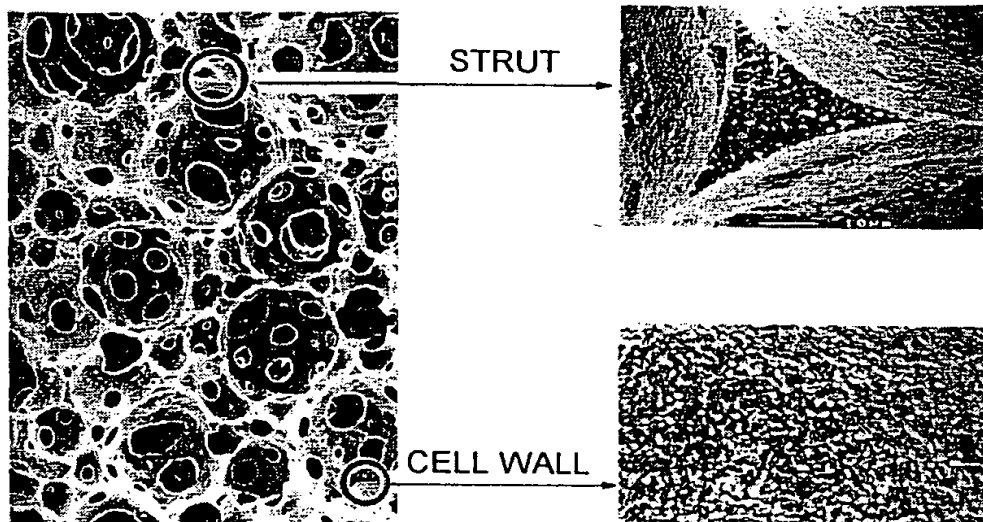


FIG. 1

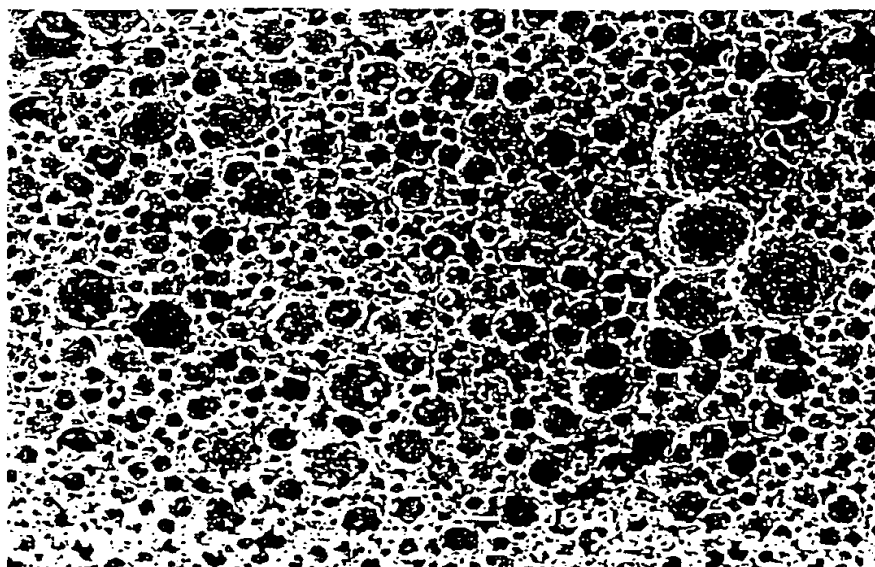


FIG. 2

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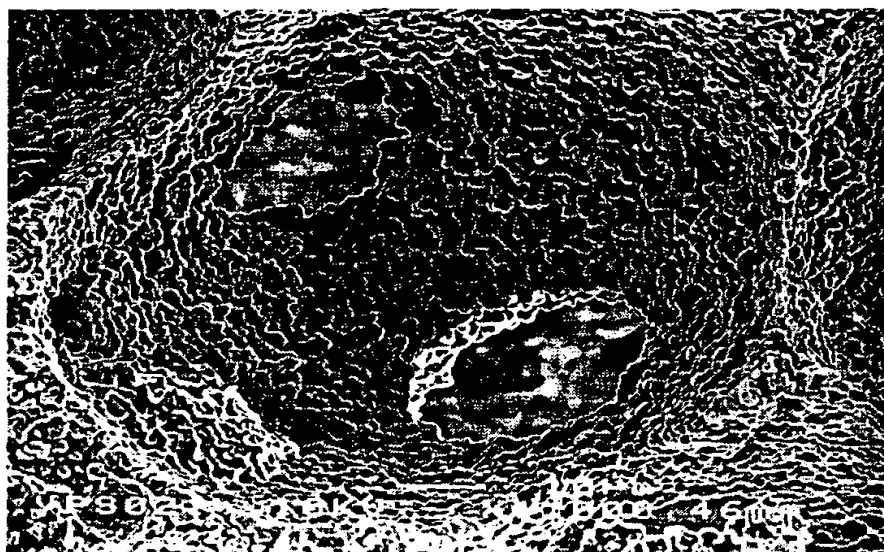


FIG. 3

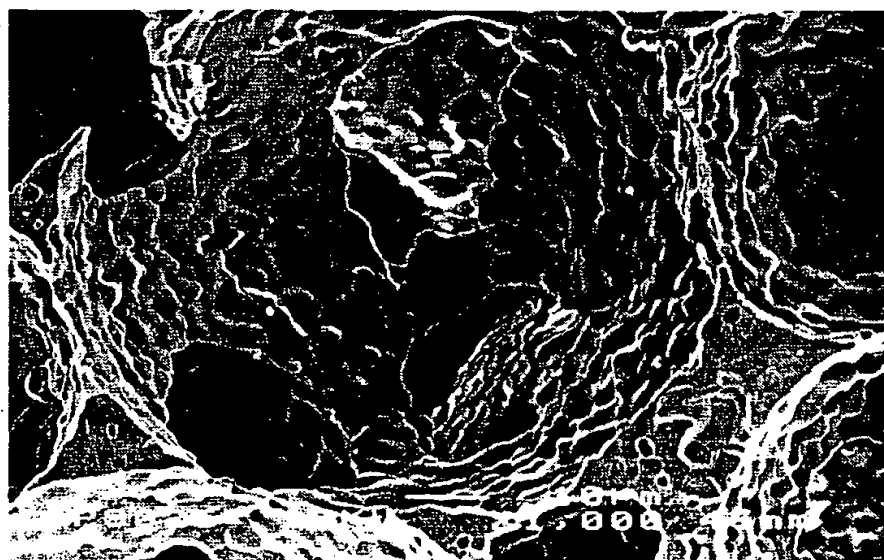


FIG. 4

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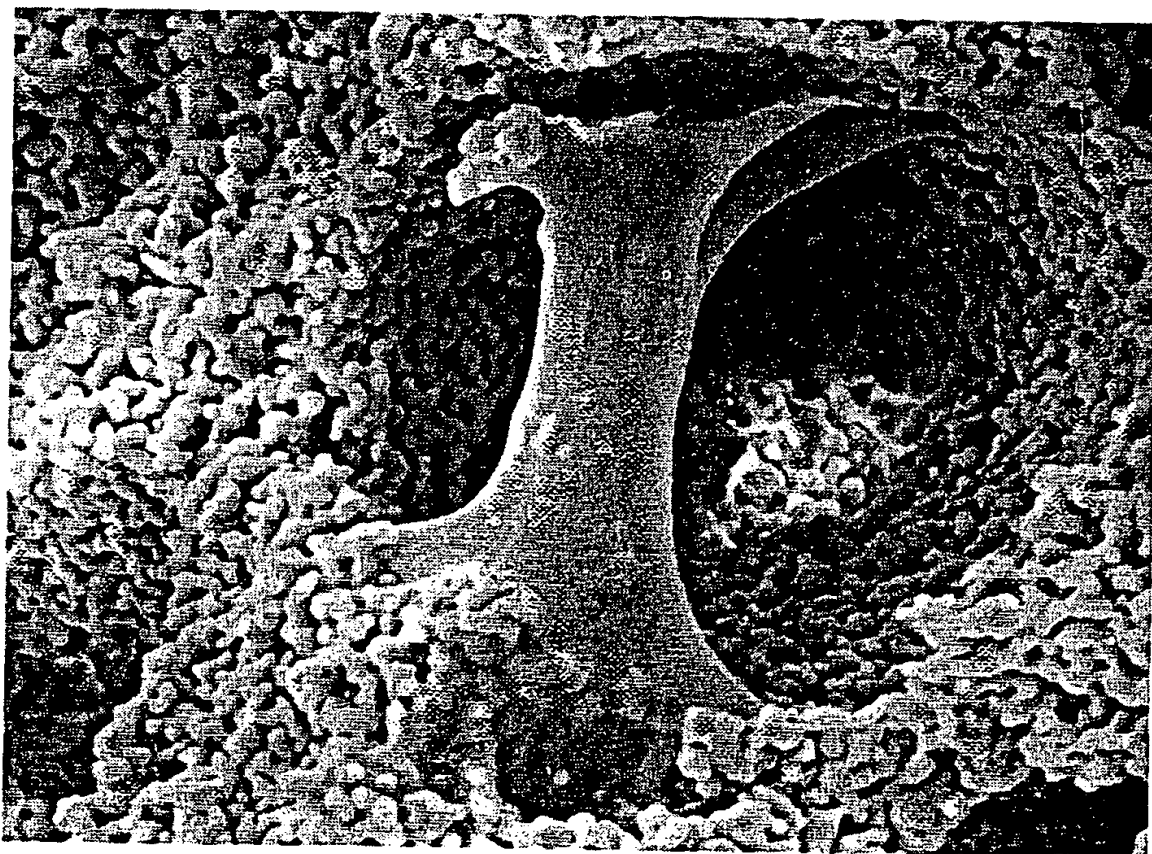


FIG. 5

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FIG. 6

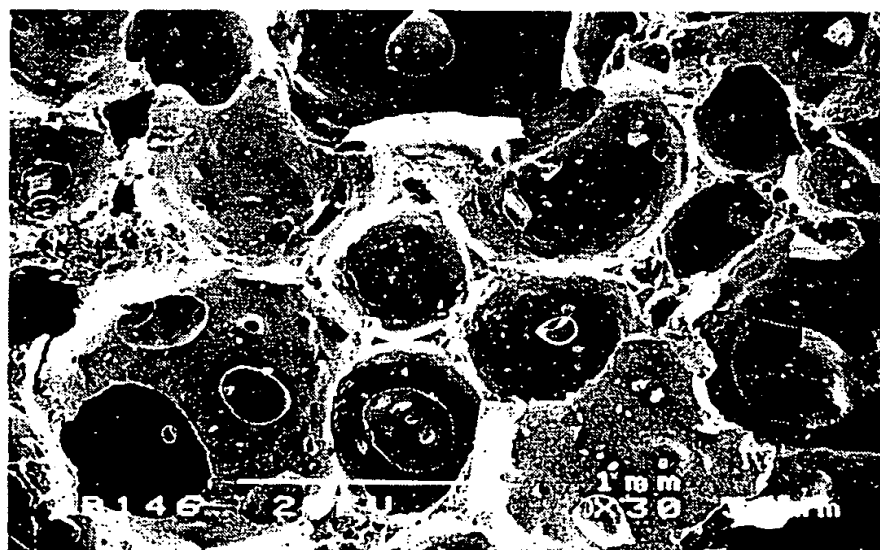


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02705

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B38/06 A61L27/00 A61K6/033 C08J9/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B A61L A61K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 04013 A (DYTECH) 4 March 1993 cited in the application see page 5, line 9 - page 6, line 13 see page 7, line 5 - page 8, line 21 see page 10, line 7-11 see page 10, line 22-25 see claims 31-46; examples IX,X ---	1-8, 10, 12, 13
A	WO 95 30631 A (DYTECH) 16 November 1995 cited in the application see claims ---	1, 3-8
A	GB 2 289 466 A (DYTECH) 22 November 1995 see claims 1, 2, 6, 9, 10 ---	1, 3-6, 8, 10, 12
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Further documents are listed in the continuation of box C.



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02705

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 9631 Derwent Publications Ltd., London, GB; Class A18, AN 96-308081 XP002035476 ANONYMOUS: "Re-oxygenation during the polymerisation of vinyl monomer MEHQ - by purging with inert gas or reducing solubility of oxygen under partial vacuum, allowing time for adequate mixing" see abstract & RESEARCH DISCLOSURE, vol. 386, no. 003, 10 June 1996, EMSWORTH, GB,</p>	9
A	<p>DE 31 08 387 A (TOYO RUBBER INDUSTRY) 21 January 1982 see page 8, line 26-26 see page 15, line 17 - line 19 see claims 1,2</p>	1,3-7,12
A	<p>US 5 011 495 A (J. O. HOLLINGER) 30 April 1991 see column 6, line 3-15; claim 1</p>	1,13,15
A	<p>US 4 218 255 A (P.K. BAJPAI) 19 August 1980 see column 5, line 15-22 see claim 1</p>	1,15
A	<p>EP 0 058 867 A (MUNDIPHARMA GMBH) 1 September 1982 see claim 1</p>	1,15
A	<p>FR 1 580 935 A (UNIROYAL) 12 September 1969 see claim 1</p>	1
A	<p>GB 2 142 919 A (SUMITOMO) 30 January 1985 see page 1, line 109-117; claim 1</p>	
A	<p>DE 43 13 715 A (RÖHM GMBH) 3 November 1994</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02705

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02705

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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*Replaced by Article 34***PRODUCTION OF POROUS ARTICLES**

The invention relates to the production of articles of controlled porosity.

In our European patent B-0598783 (Agent's ref: P00914EP) there is described and claimed a method of making a porous refractory article composed of refractory particles, the method comprising the steps of:

- a) forming a dispersion comprising particles in a liquid carrier and containing a polymerisable monomeric material
- b) introducing gas into the dispersion,
- c) polymerising the foamed structure,
- d) drying, to remove the liquid carrier to provide a solid article having pores derived from the bubbles; and
- e) firing to remove the organic binder and to provide a ceramic bond.

Preferably the monomeric material is selected to polymerise by cross linking, whereby the liquid carrier and ceramic particles are held within the polymerised structure.

The method of this prior patent is arranged to produce a variety of useful articles such as catalyst supports, flame supports; gas filters; air fresheners; ceramic armour; diesel particulate traps; insulation materials; artificial parts for the body; metal filters, reusable filters; liquid filters; storage and transportation for flammable and/or toxic materials,

humidity sensors, chromatography; filter candles for filtration of hot combustion gases, diaphragms, membranes, refractory separators, phase dividers and electrolytes for high temperature fuel cells.

In our patent publication WO95/30631 (PCT/GB95/01063, Agents Ref. P01204PCT) there is described and claimed a method of making a porous refractory article, the method comprising the steps of:

- forming an aqueous dispersion of refractory particles including a polymerisable monomer component which on polymerisation generates an exotherm
- adding a thermally activated gas generating substance
- adding agents such as initiator and/or catalyst to cause the polymerisation
- adjusting the temperature and/or pressure so that the gas generating substance generates the gas before or during the initial stage of polymerisation of the monomer component whereby the gas forms bubbles which under the heat of the exotherm interconnect to form an interconnected open pore structure.

By controlling the temperature and pressure the decomposition rate of the gas generating substance is controlled. This in turn provides a means of controlling the density of the end product.

It is one object of the invention to provide a method of making a porous article having controlled levels of porosity, interconnectivity, pore size, and mechanical properties suitable for use in various applications.

In one aspect the invention provides a method of making a porous article composed of bonded particles, the method comprising the steps of:

- a) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
- b) forming a foam of the dispersion;
- c) polymerising the foamed structure;
- d) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles, and
- e) firing the article to remove the organic binder and provide a ceramic bond

characterised in that small bubbles of gas are introduced in the dispersion with agitation to form the foam and are allowed or caused to coalesce before the polymerisation.

The dispersion comprises particles having an average particle size less than about 5 micrometres and preferably 95% of the particles will be less than about 2 micrometres.

If the particles are larger than this size than the particles tend to settle or sediment. However, the particles can be much larger, say 100 micrometres or more, in which case agents will be present to control undesired settling; polymerisation of monomers is a suitable means of preventing settling. The particles will be chosen according to the intended end use. As will be explained later, for the preferred use hydroxyapatite is present either alone or with other particles. The other particles can include both oxides and non-oxides such as alumina, mullite, silicon carbide, silicon nitride, zirconia, titanium oxide and the like.

The content of the solids in the dispersion will tend to be about 10% by weight as a minimum and about 90% by weight as a maximum; a preferred range is from about 40% to about 80% by weight.

Conveniently the liquid carrier is water but it may be organic, e.g. alcohol, glycol or the like; or a mixture.

In order to produce a dispersion with the required solids loading and a suitable rheology, it is preferred to add dispersing agents to the suspension. The dispersing agents are commonly used throughout the ceramic industry and suitable agents in each case can be determined by the man skilled in the art. The colloidal stability may be controlled by the adjustment of the pH, in addition to or alternating to the dispersion agents.

CLAIMS

1. A method of making a porous article composed of bonded particles (such as hydroxyapatite or the like) the method comprising the steps of:
 - a) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
 - b) forming a foam of the dispersion;
 - c) polymerising the foamed structure;
 - d) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles, and
 - e) firing the article to remove the organic binder and provide a ceramic bond

characterised in that small bubbles of gas are introduced in the dispersion with agitation to form the foam and are allowed to caused to coalesce before the polymerisation of the monomeric material.
2. A method according to Claim 1, wherein the dispersion comprises particles having an average particle size less than 5 micrometres and preferably 95% of the particles are less than 2 micrometres.

3. A method according to Claim 1 or 2, wherein the particles are hydroxyapatite, oxides and non-oxides such as alumina, mullite, silicon carbide, silicon nitride, zirconia, titanium oxide; and the like.
4. A method according to any preceding Claim, wherein the content of the solids in the dispersion is 10% to 90% by weight.
5. A method according to Claim 4, wherein the content of solids is 40% to 80% by weight.
6. A method according to any preceding Claim, wherein the liquid carrier is water or organic liquid or a mixture.
7. A method according to any preceding Claim, including the step of adding a dispersing agent to the dispersion.
8. A method according to any preceding Claim including the step of controlling the onset of polymerisation by adjustment of the addition levels of the initiator and catalyst for polymerisation of the monomer.
9. A method according to any preceding Claim, wherein the onset of polymerisation is controlled by adjustment of the concentration of oxygen.
10. A method according to Claim 8 or 9, wherein the period until onset of polymerisation is between an instantaneous polymerisation and 20 minutes.
11. A method according to any preceding Claim, including the step of applying a partial vacuum to a foam before the commencement of polymerisation until

after the end of polymerisation, after which the foam is brought back to atmospheric pressure.

12. A method according to any preceding Claim, wherein the product is subjected to drying and firing to form a porous ceramic article.
13. A method according to Claim 12, including the subsequent step of growing bone cells in the porous ceramic product.
14. A method according to Claim 12, wherein the ceramic article has pore sizes greater than 150 micrometres.
15. A method according to Claim 12, including adding a drug to the pores of the article.
16. A method of making a porous article composed of bonded particles, the method comprising the steps of:
 - a) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
 - b) forming a foam dispersion;
 - c) polymerising the foamed structure;
 - d) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles, and

- e) firing the article to remove the organic binder and provide a ceramic bond

characterised in that small bubbles of gas are introduced in the dispersion with agitation to form the foam and are allowed or caused to coalesce before the polymerisation, and in that the firing is carried out at a temperature appropriate to the growth of bone cells.

PATENT COOPERATION TREATY

REC'D 17 FEB 1999

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PO1885PCT	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)
International application No. PCT/GB97/02705	International filing date (day/month/year) 01/10/1997	Priority date (day/month/year) 04/10/1996	
International Patent Classification (IPC) or national classification and IPC C04B38/06			
Applicant DYTECH CORPORATION LTD. et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
 2. This REPORT consists of a total of 5 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 30/04/1998	Date of completion of this report <div style="text-align: right; font-size: 1.2em;">15. 02. 99</div>
Name and mailing address of the IPEA/ <div style="display: flex; align-items: center;"> <div> European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465 </div> </div>	Authorized officer Harbron, J Telephone No. (+49-89) 2399-8453



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB97/02705

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

5-14	as originally filed		
1-4	as received on	24/12/1998	with letter of 15/12/1998

Claims, No.:

1-10	as received on	24/12/1998	with letter of 15/12/1998
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Drawings, sheets:

1/7-7/7	as originally filed
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2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB97/02705

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-10
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-10
Industrial applicability (IA)	Yes:	Claims	1-10
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The amendments are considered to be allowable (Article 19(2) PCT).
2. Reference is made to the following documents:

D1: GB-A-2289466
D2: WO-A-9304013
3. The subject-matter of new claim 1 refers to a method for making a porous article comprised of bonded particles, the method comprising: forming a dispersion of liquid carrier, monomeric material and particles; adding a surfactant then introducing bubbles of gas, with agitation, to form a foam and allowing the bubbles to coalesce to form cells and struts; polymerising the monomeric material, drying and firing the thus-produced article.

None of the cited documents disclose all the features of claim 1 so that the subject-matter of this claim appears to be novel (Article 33 PCT).

4. The document D1 is regarded as being the closest prior art to the subject-matter of claim 1, and shows a method of making a ceramic article by forming a dispersion of water, ceramic particles and polymerisable monomer, adding a thermally decomposable gas generating substance, agitating and polymerising the monomer, removing the water and heating the product (claim 1). Although no reference is made to forming a porous article having the cells and struts of claim 1 of the present application, the method of making the articles appears to be the same as that of the present application. The use of a surfactant is also stated in D1 (examples).

One object of the present invention is to provide a method of making a porous article having controlled levels of porosity. This is achieved by adding a surfactant in a concentration according to the desired density of the porous article (claim 1). The solution to the problem cannot be considered to involve an inventive step since the solution is already known from D1 (examples) and D2 (page 8, third paragraph). Furthermore, the wide ranges of porosity and pore size presented in claim 1 do not appear to indicate any particular inventive activity. These values are also anticipated by D2 (examples) as are the firing temperatures of dependent claim 7.

Therefore the subject-matter of claim 1 is not considered to have an inventive

step.

5. Dependent claims 2-6, 8-10 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, the reasons being the same as those put forward in the preliminary opinion.

Re Item VIII

Certain observations on the international application

1. Claim 1 does not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The following functional statements do not enable the skilled person to determine which technical features are necessary to perform the stated functions: "adding a surfactant in a concentration according to the desired density of the porous article".

CLAIMS

1. A method of making a porous article comprised of bonded particles, the method comprising the steps of:
 - 1) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
 - 2) adding a surfactant in a concentration according to the desired density of the porous article and then introducing bubbles of gas with agitation to form a foam and allowing or causing the bubbles to coalesce to form cells some of which form struts;
 - 3) polymerising the monomeric material;
 - 4) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles; and
 - 5) firing the article to provide a ceramic bond and to remove organic material present, whereby the porous article formed has a porosity of 20% to 95% and comprises cell walls and struts defining pores of pore sizes in the range of 15 to 150 micrometres.
2. A method according to Claim 1, wherein the cells of the foam are adjusted to provide pore sizes greater than 150 micrometres.

3. A method according to Claim 1 or 2, including the step of controlling the onset of polymerisation by adjustment of the addition levels of the initiator and catalyst for polymerisation of the monomer to influence the growth of the foam structure.
4. A method according to Claims 1, 2 or 3, wherein the onset of polymerisation is controlled by adjustment of the concentration of oxygen to influence the growth of the foam structure.
5. A method according to Claim 4, wherein the period until onset of polymerisation is between an instantaneous polymerisation and 20 minutes.
6. A method according to any preceding Claim, including the step of applying a partial vacuum to a foam before the commencement of polymerisation until after the end of polymerisation, after which the foam is brought back to atmospheric pressure to increase the size of cells in the foam.
7. A method according to any preceding Claim, wherein the firing is carried out at 1250°C or 1350°C for two hours.
8. A method according to any preceding Claim, wherein the particles are hydroxyapatite.
9. A method according to any preceding Claim, including the subsequent step of growing bone cells in the porous ceramic product.

10. A method according to any of Claims 1 to 8, including adding a drug to the pores of the article.

LS/DAS/15.12.98
P1885.CLAIMS

PRODUCTION OF POROUS ARTICLES

The invention relates to the production of articles of controlled porosity.

In our European patent B-0598783 (Agent's ref: P00914EP) there is described and claimed a method of making a porous refractory article composed of refractory particles, the method comprising the steps of:

- a) forming a dispersion comprising particles in a liquid carrier and containing a polymerisable monomeric material
- b) introducing gas into the dispersion.
- c) polymerising the foamed structure,
- d) drying, to remove the liquid carrier to provide a solid article having pores derived from the bubbles; and
- e) firing to remove the organic binder and to provide a ceramic bond.

Preferably the monomeric material is selected to polymerise by cross linking, whereby the liquid carrier and ceramic particles are held within the polymerised structure. In that disclosure there is mention that surfactants may be added to the dispersion to prevent premature settling of solids in the dispersion or to control the foaming characteristics. In Example IX Teepol surfactant is added to the dispersion. The foam was allowed to polymerise and ultimately sintered at 1450°C for two hours.

The method of this prior patent is arranged to produce a variety of useful articles such as catalyst supports, flame supports; gas filters; air fresheners; ceramic armour; diesel particulate traps; insulation materials; artificial parts for the body; metal filters, reusable filters; liquid filters; storage and transportation for flammable and/or toxic materials, humidity sensors, chromatography; filter candles for filtration of hot combustion gases, diaphragms, membranes, refractory separators, phase dividers and electrolytes for high temperature fuel cells.

In our patent publication WO95/30631 (PCT/GB95/01063, Agents Ref. P01204PCT) there is described and claimed a method of making a porous refractory article, the method comprising the steps of:

- forming an aqueous dispersion of refractory particles including a polymerisable monomer component which on polymerisation generates an exotherm
- adding a thermally activated gas generating substance
- adding agents such as initiator and/or catalyst to cause the polymerisation
- adjusting the temperature and/or pressure so that the gas generating substance generates the gas before or during the initial stage of polymerisation of the monomer component whereby the gas forms bubbles which under the heat of the exotherm interconnect to form an interconnected open pore structure.

By controlling the temperature and pressure the decomposition rate of the gas generating substance is controlled. This in turn provides a means of controlling the density of the end product. In this disclosure TRITON X-100, a surfactant was added as the last ingredient to the dispersion to stabilise the foam.

It is one object of the invention to provide a method of making a porous article having controlled levels of porosity, interconnectivity, pore size, and mechanical properties suitable for use in various applications.

In one aspect the invention provides a method of making a porous article comprised of bonded particles, the method comprising the steps of:

- 1) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
- 2) adding a surfactant in a concentration according to the desired density of the porous article and then introducing bubbles of gas with agitation to form a foam and allowing or causing the bubbles to coalesce to form cells some of which form struts;
- 3) polymerising the monomeric material;

- 4) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles; and
- 5) firing the article to provide a ceramic bond and to remove organic material present, whereby the porous article formed has a porosity of 20% to 95% and comprises cell walls and struts defining pores of pore sizes in the range of 15 to 150 micrometres.

The dispersion comprises particles having an average particle size less than about 5 micrometres and preferably 95% of the particles will be less than about 2 micrometres.

LS/BW/P01885PCT

December 15, 1998

European Patent Office
Erhardstrasse 27
D-80298 Munchen 2
Germany

BY FAX TO:
00.49.89.23994465

For the attention of Examiner J HARBRON

Dear Sirs

DYTECH CORPORATION
International patent application PCT/GB97/02705
Our Ref: P01885PCT

I refer to the Communication under Chapter II and now file:

- i) a new set of Claims and
- ii) new pages of description which have statements of invention and acknowledge the prior art.

I look forward to having the examination report.

Please datestamp and return the extra copy of this letter to show safe receipt.

Yours faithfully

CLAIMS

1. A method of making a porous article comprised of bonded particles, the method comprising the steps of:
 - 1) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
 - 2) adding a surfactant in a concentration according to the desired density of the porous article and then introducing bubbles of gas with agitation to form a foam and allowing or causing the bubbles to coalesce to form cells some of which form struts;
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2. A method according to Claim 1, wherein the cells of the foam are adjusted to provide pore sizes greater than 150 micrometres.

3. A method according to Claim 1 or 2, including the step of controlling the onset of polymerisation by adjustment of the addition levels of the initiator and catalyst for polymerisation of the monomer to influence the growth of the foam structure.
4. A method according to Claims 1, 2 or 3, wherein the onset of polymerisation is controlled by adjustment of the concentration of oxygen to influence the growth of the foam structure.
5. A method according to Claim 4, wherein the period until onset of polymerisation is between an instantaneous polymerisation and 20 minutes.
6. A method according to any preceding Claim, including the step of applying a partial vacuum to a foam before the commencement of polymerisation until after the end of polymerisation, after which the foam is brought back to atmospheric pressure to increase the size of cells in the foam.
7. A method according to any preceding Claim, wherein the firing is carried out at 1250°C or 1350°C for two hours.
8. A method according to any preceding Claim, wherein the particles are hydroxyapatite.
9. A method according to any preceding Claim, including the subsequent step of growing bone cells in the porous ceramic product.

10. A method according to any of Claims 1 to 8, including adding a drug to the pores of the article.

LS/DAS/15.12.98
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- a) forming a dispersion comprising particles in a liquid carrier and containing a polymerisable monomeric material
- b) introducing gas into the dispersion,
- c) polymerising the foamed structure,
- d) drying, to remove the liquid carrier to provide a solid article having pores derived from the bubbles; and
- e) firing to remove the organic binder and to provide a ceramic bond.

Preferably the monomeric material is selected to polymerise by cross linking, whereby the liquid carrier and ceramic particles are held within the polymerised structure. In that disclosure there is mention that surfactants may be added to the dispersion to prevent premature settling of solids in the dispersion or to control the foaming characteristics. In Example IX Teepol surfactant is added to the dispersion. The foam was allowed to polymerise and ultimately sintered at 1450⁰C for two hours.

The method of this prior patent is arranged to produce a variety of useful articles such as catalyst supports, flame supports; gas filters; air fresheners; ceramic armour; diesel particulate traps; insulation materials; artificial parts for the body; metal filters, reusable filters; liquid filters; storage and transportation for flammable and/or toxic materials, humidity sensors, chromatography; filter candles for filtration of hot combustion gases, diaphragms, membranes, refractory separators, phase dividers and electrolytes for high temperature fuel cells.

In our patent publication WO95/30631 (PCT/GB95/01063, Agents Ref. P01204PCT) there is described and claimed a method of making a porous refractory article, the method comprising the steps of:

- forming an aqueous dispersion of refractory particles including a polymerisable monomer component which on polymerisation generates an exotherm
- adding a thermally activated gas generating substance
- adding agents such as initiator and/or catalyst to cause the polymerisation
- adjusting the temperature and/or pressure so that the gas generating substance generates the gas before or during the initial stage of polymerisation of the monomer component whereby the gas forms bubbles which under the heat of the exotherm interconnect to form an interconnected open pore structure.

By controlling the temperature and pressure the decomposition rate of the gas generating substance is controlled. This in turn provides a means of controlling the density of the end product. In this disclosure TRITON X-100, a surfactant was added as the last ingredient to the dispersion to stabilise the foam.

It is one object of the invention to provide a method of making a porous article having controlled levels of porosity, interconnectivity, pore size, and mechanical properties suitable for use in various applications.

In one aspect the invention provides a method of making a porous article comprised of bonded particles, the method comprising the steps of:

- 1) forming a dispersion comprising a liquid carrier and the particles and a polymerisable monomeric material;
- 2) adding a surfactant in a concentration according to the desired density of the porous article and then introducing bubbles of gas with agitation to form a foam and allowing or causing the bubbles to coalesce to form cells some of which form struts;
- 3) polymerising the monomeric material;

- 4) drying the structure to remove the liquid carrier and provide a solid article having pores derived from the bubbles; and
- 5) firing the article to provide a ceramic bond and to remove organic material present, whereby the porous article formed has a porosity of 20% to 95% and comprises cell walls and struts defining pores of pore sizes in the range of 15 to 150 micrometres.

The dispersion comprises particles having an average particle size less than about 5 micrometres and preferably 95% of the particles will be less than about 2 micrometres.

TENT COOPERATION TRA

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

SHAW, Laurence
LAURENCE SHAW & ASSOCIATES
5th Floor, Metropolitan House
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ETATS-UNIS D'AMERIQUE

PO1885 PCT
PCT TB LS

NOTIFICATION CONCERNING INFORMAL
COMMUNICATIONS WITH THE APPLICANT

(PCT Rule 66.6)

Date of mailing
(day/month/year)

- 9. 12. 98

Applicant's or agent's file reference

PO1885PCT

TRANSMITTAL FOR INFORMATION

International application no.

PCT/GB97/02705

International filing date (day/month/year)

01/10/1997

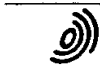
Applicant

DYTECH CORPORATION LTD. et al.

An informal communication took place on 01/12/1998, between the International Preliminary Examining Authority and the applicant / the agent.

A copy of the note on that communication (Form PCT/IPEA/428) is herewith transmitted for your information.

Name and mailing address of the international
preliminary examining authority



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Vertrag über die internationale Zusammenarbeit auf dem Gebiet des Patentwesens
Patent Cooperation Treaty
Traité de coopération en matière de brevets

PCT

Application No.:

PCT/GB97/02705

Note on a personal informal communication with the Applicant

A copy of this note is being sent to the Applicant for information

Participants

Agent: Laurence Shaw, assisted by Werner Mukelka

The identity of the representative has been checked

Examiner(s): Harbron, J

Summary of the communication

The interview commenced at 14:00 on Tuesday, December 1st. 1998.

Opening remarks:

A check was made that the dossier in question was indeed the relevant one due to a discrepancy in the dossier number.

The representative explained a little of the history of the application particularly with reference to documents D1 and D2 (both filed by the applicant) wherein D2 was the parent patent and D1 a variation thereof, whose main feature was stated to be in-situ gas generation.

The main feature of the present application was stated to be porosity control of the products in question.

The main features discussed were:

the possibility of further characteristics being introduced into claim 1 such as a surfactant or a reference to the interior structure of the products in question;

maintenance of the claims in the two-part form;

methods of removing the clarity objection to claim 16 were discussed such as use of the

Vertrag über die internationale Zusammenarbeit auf dem Gebiet des Patentwesens
Patent Cooperation Treaty
Traité de coopération en matière de brevets

PCT

Application No.:

PCT/GB97/02705

term "undersintered" or specifying the sintering conditions.

concern was raised by the representative about a possible lack of unity objection with regard to claims 1 and 16.

Minor clarity objections were made by the examiner with regard to claim 1 namely, the lack of antecedent for the reference to "the bubbles" (part d)), the unsupported reference to "the organic binder", and also to the use of the relative term in the expression "small bubbles of gas" in the characterizing portion of the claim.

01/12/1998

.....
Date (day / month / year)



Harbron, J

.....
Authorized officer of IPEA

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

SHAW, Laurence
LAURENCE SHAW & ASSOCIATES
5th Floor, Metropolitan House
1 Hagley Road
Edgbaston
Birmingham B16 8TG
ETATS-UNIS D'AMERIQUE

PO1885PCT

PCT

WRITTEN OPINION

(PCT Rule 66)
17 AUG 1998

Date of mailing (day/month/year) 6-08-98

Applicant's or agent's file reference

PO1885PCT

REPLY DUE

within 3 month(s)

from the above date of mailing

6-19-98

International application no.

PCT/GB97/02705

International filing date (day/month/year)

01/10/1997

Priority date (day/month/year)

04/10/1996

International Patent Classification (IPC) or both national classification and IPC

C04B38/06

Applicant

DYTECH CORPORATION LTD. et al.

1. This written opinion is the **first** drawn up by this International Preliminary Examining Authority.
2. This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☒ Certain documents cited
 - VII ☒ Certain defects in the international application
 - VIII ☒ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and / or arguments, see Rule 66.4bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 04/02/1999

Name and mailing address of the international preliminary examining authority



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
Fax: (+49-89) 2399-4465

Authorized officer / Examiner
Harbron, J

Formalities officer (incl. extension of time limits)
Durany Rivera, A
Telephone No. (+49-89) 2399-8114



WRITTEN OPINION

International application No. PCT/GB97/02705

I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*).

Description, pages:

1-14 as originally filed

Claims, No.:

1-16 as originally filed

Drawings, sheets:

1/7-7/7 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims	1, 3-7, 11-12 No. 9, 13-15 Yes
Inventive step (IS)	Claims	2, 8 No
Industrial applicability (IA)	Claims	1-15 Yes

2. Citations and explanations

see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item I

Basis of the opinion

The examination is being carried out on the **following application documents:**

Text for the Contracting States:

AT BE CH DE DK ES FI FR GB GR IT IE LI LU MC NL PT SE

Description, pages:

1-14 as originally filed

Claims, No.:

1-16 as originally filed

Drawings, sheets:

1/7-7/7 as originally filed

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Rule 66.2(a)(ii) Novelty, inventive step and industrial applicability.

Reference is made to the following documents:

D1: GB-A-2289466

D2: WO-A-9304013
D3: WPI Database, RD-A-386003
D4: US-A-5011495
D5: US-A-4218255

Document D1 discloses a process for producing porous ceramic articles by forming an aqueous dispersion of ceramic particles and a polymerisable monomer, adding a thermally decomposable gas generating substance, adding agents such as initiator and/or catalyst, and, finally, adjusting temperature or pressure so that gas is generated before or during the initial stage of polymerisation to form bubbles which interconnect to form an interconnected open pore structure (claim 1).

This process appears to be essentially the same as that of the subject-matter of claims 1 and 16 (but see point VIII) of the current application which, consequently, is not considered to be novel.

2. Dependent claims 3-7, 11-12 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty, the reasons being as follows:
 - 2.1. The ceramic materials and their preferred amounts (claims 3-5) in the slurry are referred to in the examples of D1.
 - 2.2. The use of an aqueous dispersion (claim 6) is known from claim 1 of D1.
 - 2.3. Addition of a dispersing agent (claim 7) is known from the examples of D1.
 - 2.4. The use of a partial vacuum before polymerisation (claim 11) is anticipated by claim 2 of D1.
 - 2.5. Drying and firing of the product (claim 12) is known from Example II of D1.
3. Inventive step.
 - 3.1. The features of dependent claim 2 (particle size) have already been employed for the same purpose in a similar slurry, see document D2, page 5, lines 13-15. It would therefore be obvious to the person skilled in the art, to apply these features with corresponding effect to a slurry according to document D1, thereby arriving at a slurry according to claims 1 and 2.
 - 3.2. Similarly, the polymer initiator featured in dependent claim 8 is known from

D2 (Example IX) and would be an obvious choice for the skilled man.

3.3 The feature of dependent claim 9 would also be obvious to the skilled man in the light of the teaching of D3.

3.4 The features of claims 13 and 14 are known from D4 (claims) and that of claim 15 from D5 (column 4, lines 37-48) and would also be obvious options for the skilled man.

Re Item VII

Certain defects in the international application

The term "Bioglass" appearing on page 9, line 2 of the application would appear to be a registered trademark but is not designated as such.

Re Item VIII

Certain observations on the international application

Independent claim 16 refers to a method of making a porous article...characterised in that the firing is carried out at a temperature appropriate to the growth of bone cells. It is not clear how the sintering temperature of an article would be appropriate to the growth of bone cells, nor is such a temperature or temperature range disclosed in the application.

In view of the above, no definite meaning is attached to the expression "appropriate to the growth of bone cells" in the present context and therefore this expression is not regarded as representing a limiting feature of claim 16.



✉ EPA/EPO/OEB
D-80298 München
☎ (089) 2399-0
TX 523 656 eprmu d
FAX (089) 2399-4465

**Europäisches
Patentamt**

Generaldirektion 2

**European
Patent Office**

Directorate General 2

**Office européen
des brevets**

Direction Générale 2

Correspondence with the EPO on PCT Chapter II demands

In order to ensure that your PCT Chapter II demand is dealt with as promptly as possible you are requested to use the enclosed self-adhesive labels with any correspondence relating to the demand sent to the Munich Office.

One of these labels should be affixed to a prominent place in the upper part of the letter or form etc. which you are filing.

PATENT COOPERATION TREATY

Donoff

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: SHAW, Laurence LAURENCE SHAW & ASSOCIATES 5th Floor, Metropolitan House 1 Hagley Road Edgbaston Birmingham B16 8TG ETATS-UNIS D'AMERIQUE	<div style="border: 1px solid black; padding: 5px; display: inline-block;"> FILE NO. FOR - 2 MAR 1999 </div>	PO1885 PCT SELS	PCT NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)
Applicant's or agent's file reference PO1885PCT		Date of mailing (day/month/year)	
International application No. PCT/GB97/02705		International filing date (day/month/year) 01/10/1997	Priority date (day/month/year) 04/10/1996
Applicant DYTECH CORPORATION LTD. et al.			

15. 02. 99

IMPORTANT NOTIFICATION

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/ <div style="display: flex; align-items: center;"> <div> European Patent Office D-80298 Munich Tel. (+49-89) 2399-0. Tx: 523656 epmu d Fax: (+49-89) 2399-4465 </div> </div>	Authorized officer Durany Rivera, A Tel. (+49-89) 2399-8114
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PO1885PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)	
International application No. PCT/GB97/02705	International filing date (day/month/year) 01/10/1997	Priority date (day/month/year) 04/10/1996
International Patent Classification (IPC) or national classification and IPC C04B38/06		
Applicant DYTECH CORPORATION LTD. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 30/04/1998	Date of completion of this report 15.02.99
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Harbron, J Telephone No. (+49-89) 2399-8453 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB97/02705

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

5-14	as originally filed		
1-4	as received on	24/12/1998	with letter of 15/12/1998

Claims, No.:

1-10	as received on	24/12/1998	with letter of 15/12/1998
------	----------------	------------	---------------------------

Drawings, sheets:

1/7-7/7	as originally filed
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2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB97/02705

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-10
	No: Claims
Inventive step (IS)	Yes: Claims
	No: Claims 1-10
Industrial applicability (IA)	Yes: Claims 1-10
	No: Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The amendments are considered to be allowable (Article 19(2) PCT).
2. Reference is made to the following documents:

D1: GB-A-2289466
D2: WO-A-9304013
3. The subject-matter of new claim 1 refers to a method for making a porous article comprised of bonded particles, the method comprising: forming a dispersion of liquid carrier, monomeric material and particles; adding a surfactant then introducing bubbles of gas, with agitation, to form a foam and allowing the bubbles to coalesce to form cells and struts; polymerising the monomeric material, drying and firing the thus-produced article.

None of the cited documents disclose all the features of claim 1 so that the subject-matter of this claim appears to be novel (Article 33 PCT).

4. The document D1 is regarded as being the closest prior art to the subject-matter of claim 1, and shows a method of making a ceramic article by forming a dispersion of water, ceramic particles and polymerisable monomer, adding a thermally decomposable gas generating substance, agitating and polymerising the monomer, removing the water and heating the product (claim 1). Although no reference is made to forming a porous article having the cells and struts of claim 1 of the present application, the method of making the articles appears to be the same as that of the present application. The use of a surfactant is also stated in D1 (examples).

One object of the present invention is to provide a method of making a porous article having controlled levels of porosity. This is achieved by adding a surfactant in a concentration according to the desired density of the porous article (claim 1). The solution to the problem cannot be considered to involve an inventive step since the solution is already known from D1 (examples) and D2 (page 8, third paragraph). Furthermore, the wide ranges of porosity and pore size presented in claim 1 do not appear to indicate any particular inventive activity. These values are also anticipated by D2 (examples) as are the firing temperatures of dependent claim 7.

Therefore the subject-matter of claim 1 is not considered to have an inventive

step.

5. Dependent claims 2-6, 8-10 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, the reasons being the same as those put forward in the preliminary opinion.

Re Item VIII

Certain observations on the international application

1. Claim 1 does not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The following functional statements do not enable the skilled person to determine which technical features are necessary to perform the stated functions: "adding a surfactant in a concentration according to the desired density of the porous article".

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

P01885 PCT
SCLS

PCT

To:

Laurence SHAW & ASSOCIATES
Attn. SHAW, Laurence
5th Floor, Metropolitan House
1 Hagley Road, Edgbaston
BIRMINGHAM B16 8TG
UNITED KINGDOM

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

23 JAN 1998

(PCT Rule 44.1)

Date of mailing
(day/month/year)

26/01/1998

Applicant's or agent's file reference

P01885PCT

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/GB 97/02705

International filing date

(day/month/year)

01/10/1997

Applicant

DYTECH CORPORATION LTD et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicants's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Alex Schmidt

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference P01885PCT	FOR FURTHER ACTION		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/GB 97/ 02705	International filing date (day/month/year) 01/10/1997	(Earliest) Priority Date (day/month/year) 04/10/1996	
Applicant DYTECH CORPORATION LTD et al.			

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable(see Box I).

2. ☐ Unity of Invention is lacking(see Box II).

3. ☐ The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing

☐ filed with the international application.

☐ furnished by the applicant separately from the international application,

☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.

☐ Transcribed by this Authority

4. With regard to the title, ☒ the text is approved as submitted by the applicant

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is:

Figure No. --- ☐ as suggested by the applicant.

☐ None of the figures.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/02705

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B38/06 A61L27/00 A61K6/033 C08J9/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B A61L A61K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 04013 A (DYTECH) 4 March 1993 cited in the application see page 5, line 9 - page 6, line 13 see page 7, line 5 - page 8, line 21 see page 10, line 7-11 see page 10, line 22-25 see claims 31-46; examples IX,X ---	1-8, 10, 12, 13
A	WO 95 30631 A (DYTECH) 16 November 1995 cited in the application see claims ---	1, 3-8
A	GB 2 289 466 A (DYTECH) 22 November 1995 see claims 1, 2, 6, 9, 10 ---	1, 3-6, 8, 10, 12
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

19 January 1998

Date of mailing of the international search report

26/01/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Daeleman, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/02705

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 9631 Derwent Publications Ltd., London, GB; Class A18, AN 96-308081 XP002035476 ANONYMOUS: "Re-oxygenation during the polymerisation of vinyl monomer MEHQ - by purging with inert gas or reducing solubility of oxygen under partial vacuum, allowing time for adequate mixing" see abstract & RESEARCH DISCLOSURE, vol. 386, no. 003, 10 June 1996, EMSWORTH, GB,</p>	9
A	<p>DE 31 08 387 A (TOYO RUBBER INDUSTRY) 21 January 1982 see page 8, line 26-26 see page 15, line 17 - line 19 see claims 1,2</p>	1,3-7,12
A	<p>US 5 011 495 A (J. O. HOLLINGER) 30 April 1991 see column 6, line 3-15; claim 1</p>	1,13,15
A	<p>US 4 218 255 A (P.K. BAJPAI) 19 August 1980 see column 5, line 15-22 see claim 1</p>	1,15
A	<p>EP 0 058 867 A (MUNDIPHARMA GMBH) 1 September 1982 see claim 1</p>	1,15
A	<p>FR 1 580 935 A (UNIROYAL) 12 September 1969 see claim 1</p>	1
A	<p>GB 2 142 919 A (SUMITOMO) 30 January 1985 see page 1, line 109-117; claim 1</p>	
A	<p>DE 43 13 715 A (RÖHM GMBH) 3 November 1994</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02705

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9304013 A	04-03-93	AT 132124 T AU 2405492 A DE 69207198 D DE 69207198 T EP 0598783 A ES 2081126 T JP 7501307 T US 5563106 A	15-01-96 16-03-93 08-02-96 25-07-96 01-06-94 16-02-96 09-02-95 08-10-96
WO 9530631 A	16-11-95	AU 2415095 A EP 0759018 A GB 2289272 A	29-11-95 26-02-97 15-11-95
GB 2289466 A	22-11-95	AU 2415195 A BR 9507674 A EP 0759020 A WO 9530633 A US 5705448 A	29-11-95 19-08-97 26-02-97 16-11-95 06-01-98
DE 3108387 A	21-01-82	JP 56145153 A CA 1158424 A US 4472332 A	11-11-81 13-12-83 18-09-84
US 5011495 A	30-04-91	NONE	
US 4218255 A	19-08-80	NONE	
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